

**PHOTOCATALYTIC REMOVAL OF METHYLENE  
BLUE USING IMMOBILIZED TRANSITION  
METALS DOPED TITANIUM DIOXIDE ON  
GLASS AND GRANULAR ACTIVATED CARBON**



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UNIVERSITI MALAYSIA SABAH

**SCHOOL OF SCIENCE AND TECHNOLOGY  
UNIVERSITI MALAYSIA SABAH  
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THE DEGREE OF MASTER OF SCIENCE**

**SCHOOL OF SCIENCE AND TECHNOLOGY  
UNIVERSITI MALAYSIA SABAH  
2009**

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## ABSTRACT

### PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE USING IMMOBILIZED TRANSITION METALS DOPED TITANIUM DIOXIDE ON GLASS AND GRANULAR ACTIVATED CARBON

Photocatalytic degradation of methylene blue (MB) dye in aqueous solution using metal-doped titania ( $\text{TiO}_2$ ) under UV-A light and in the presence of  $\text{H}_2\text{O}_2$  were investigated. The photocatalysts used were single metal-doped  $\text{TiO}_2$  (i.e.  $\text{Cr}^{3+}\text{-TiO}_2$ ,  $\text{Cu}^{2+}\text{-TiO}_2$ ,  $\text{Fe}^{3+}\text{-TiO}_2$ ,  $\text{Mo}^{5+}\text{-TiO}_2$ , and  $\text{V}^{5+}\text{-TiO}_2$ ) and dual metal-doped  $\text{TiO}_2$  (i.e.  $\text{Cr}^{3+},\text{Mo}^{5+}\text{-TiO}_2$ ,  $\text{Cr}^{3+},\text{V}^{5+}\text{-TiO}_2$ ,  $\text{Cu}^{2+},\text{Mo}^{5+}\text{-TiO}_2$ ,  $\text{Cu}^{2+},\text{V}^{5+}\text{-TiO}_2$ ,  $\text{Fe}^{3+},\text{Mo}^{5+}\text{-TiO}_2$  and  $\text{Fe}^{3+},\text{V}^{5+}\text{-TiO}_2$ ) coated on Pyrex-glass tubes, and single metal doped- $\text{TiO}_2$  (i.e.  $\text{V}^{5+}\text{-TiO}_2$ ) coated on granular activated carbon (GAC). All the catalysts were prepared in the lab and the doping/coating was done according to sol-gel dip-coating method. For comparison, undoped  $\text{TiO}_2$  coated on Pyrex-glass tube and GAC were also studied. The reactions were carried out in a photo-reactor. Subsamples of the dye solution was withdrawn at specific time intervals and its absorbance was measured at  $\lambda_{\text{max}} = 665 \text{ nm}$  using a UV-Vis spectrophotometer. The resultant dye degradation was presented as % dye removed and comparisons were made for its values at 120 minutes. The results showed that the degradation of MB using these titania-assisted systems increased with reaction time. Equilibrium, however, was not attained within 120 minutes. Amongst the single metal-doped  $\text{TiO}_2$  systems only  $\text{V}^{5+}\text{-TiO}_2$  produced greater degradation of MB compared with the undoped  $\text{TiO}_2$ . The other single metal-doped  $\text{TiO}_2$  systems ( $\text{Mo}^{5+}\text{-TiO}_2 > \text{Fe}^{3+}\text{-TiO}_2 \approx \text{Cr}^{3+}\text{-TiO}_2 \approx \text{Cu}^{2+}\text{-TiO}_2$ ) produced much lower degradation compared to undoped  $\text{TiO}_2$ . For dual metal-doped  $\text{TiO}_2$  systems, the degradation efficiency followed the order:  $\text{Cu}^{2+},\text{V}^{5+}\text{-TiO}_2 > \text{Fe}^{3+},\text{V}^{5+}\text{-TiO}_2 > \text{Cr}^{3+},\text{V}^{5+}\text{-TiO}_2 > \text{Cr}^{3+},\text{Mo}^{5+}\text{-TiO}_2 \approx \text{Fe}^{3+},\text{Mo}^{5+}\text{-TiO}_2 \approx \text{Cu}^{2+},\text{Mo}^{5+}\text{-TiO}_2$ . Only  $\text{Cu}^{2+},\text{V}^{5+}\text{-TiO}_2$  produced greater degradation of MB compared with the undoped  $\text{TiO}_2$ . However, its efficiency was lower than  $\text{V}^{5+}\text{-TiO}_2$  but higher than  $\text{Cu}^{2+}\text{-TiO}_2$ . Meanwhile the  $\text{V}^{5+}$ -doped and undoped  $\text{TiO}_2$  catalysts coated on GAC did not exhibit significant photoactivity. The removal of MB from solution by both systems was of similar magnitude to that of due to adsorption by GAC and was about 2x less efficient compared with  $\text{V}^{5+}\text{-TiO}_2$  and  $\text{TiO}_2$  coated on Pyrex-glass tubes. All the above reactions fitted well with pseudo-first-order kinetics according to the Langmuir-Hinshelwood model. Overall, among the systems investigated, photocatalytic degradation of MB is most efficient when  $\text{V}^{5+}$ -doped  $\text{TiO}_2$  coated on an inert support, namely Pyrex-glass tubes, was used.

## ABSTRAK

Degradasi fotopemangkinan pewarna metilena biru (MB) dalam larutan akueous telah dikaji dengan menggunakan titania ( $\text{TiO}_2$ ) didopkan dengan logam dalam kehadiran sinaran UV-A dan juga  $\text{H}_2\text{O}_2$ . Fotomangkin yang digunakan adalah  $\text{TiO}_2$  yang didopkan dengan logam tunggal (i.e.  $\text{Cr}^{3+}\text{-TiO}_2$ ,  $\text{Cu}^{2+}\text{-TiO}_2$ ,  $\text{Fe}^{3+}\text{-TiO}_2$ ,  $\text{Mo}^{5+}\text{-TiO}_2$ , and  $\text{V}^{5+}\text{-TiO}_2$ ) dan  $\text{TiO}_2$  didopkan dengan dwilogam (i.e.  $\text{Cr}^{3+}, \text{Mo}^{5+}\text{-TiO}_2$ ,  $\text{Cr}^{3+}, \text{V}^{5+}\text{-TiO}_2$ ,  $\text{Cu}^{2+}, \text{Mo}^{5+}\text{-TiO}_2$ ,  $\text{Cu}^{2+}, \text{V}^{5+}\text{-TiO}_2$ ,  $\text{Fe}^{3+}, \text{Mo}^{5+}\text{-TiO}_2$  and  $\text{Fe}^{3+}, \text{V}^{5+}\text{-TiO}_2$ ) dan disalutkan pada tiub kaca Pyrex, dan  $\text{TiO}_2$  yang didopkan dengan logam tunggal (i.e.  $\text{V}^{5+}\text{-TiO}_2$ ) dan disalutkan pada butiran karbon teraktif (GAC). Kesemua fotomangkin ini telah disediakan di dalam makmal dan pendopan/penyalutan dilakukan secara kaedah sol-gel dip-coating. Sebagai perbandingan,  $\text{TiO}_2$  tanpa dopan yang disalutkan pada tiub kaca Pyrex dan GAC juga turut dikaji. Tindak balas degradasi ini telah dijalankan dalam satu reaktor-foto. Subsampel larutan pewarna dikeluarkan pada jangka masa yang tertentu dan serapannya diukur pada  $\lambda_{\text{max}} = 665 \text{ nm}$  dengan menggunakan spektrofotometer UV-Vis. Degradasi pewarna diberikan sebagai % penyingkiran pewarna dan perbandingan nilai dilakukan pada 120 minit. Hasil yang diperolehi menunjukkan bahawa degradasi MB bagi sistem-sistem titania ini meningkat dengan masa tindak balas. Walau bagaimanapun, keseimbangan tidak tercapai dalam masa 120 minit. Di antara sistem-sistem  $\text{TiO}_2$  yang didopkan dengan logam tunggal, hanya  $\text{V}^{5+}\text{-TiO}_2$  menghasilkan degradasi MB yang lebih tinggi berbanding dengan  $\text{TiO}_2$  tanpa dopan. Sistem-sistem  $\text{TiO}_2$  yang didopkan dengan logam tunggal yang lain ( $\text{Mo}^{5+}\text{-TiO}_2 > \text{Fe}^{3+}\text{-TiO}_2 \approx \text{Cr}^{3+}\text{-TiO}_2 \approx \text{Cu}^{2+}\text{-TiO}_2$ ) menunjukkan degradasi yang lebih rendah berbanding dengan  $\text{TiO}_2$  tanpa dopan. Bagi sistem-sistem  $\text{TiO}_2$  yang didopkan dengan dwilogam, keberkesanan degradasi adalah mengikut urutan:  $\text{Cu}^{2+}, \text{V}^{5+}\text{-TiO}_2 > \text{Fe}^{3+}, \text{V}^{5+}\text{-TiO}_2 > \text{Cr}^{3+}, \text{V}^{5+}\text{-TiO}_2 > \text{Cr}^{3+}, \text{Mo}^{5+}\text{-TiO}_2 \approx \text{Fe}^{3+}, \text{Mo}^{5+}\text{-TiO}_2 \approx \text{Cu}^{2+}, \text{Mo}^{5+}\text{-TiO}_2$ . Hanya  $\text{Cu}^{2+}, \text{V}^{5+}\text{-TiO}_2$  menghasilkan degradasi MB yang lebih tinggi berbanding dengan  $\text{TiO}_2$  tanpa dopan. Walau bagaimanapun, keberkesananannya adalah lebih rendah daripada  $\text{V}^{5+}\text{-TiO}_2$  tetapi lebih tinggi daripada  $\text{Cu}^{2+}\text{-TiO}_2$ . Sementara itu, fotomangkin  $\text{TiO}_2$  yang didopkan dengan  $\text{V}^{5+}$  dan  $\text{TiO}_2$  tanpa dopan disalutkan pada GAC tidak menunjukkan aktiviti-foto yang signifikan. Penyingkiran MB dari larutan oleh kedua-dua sistem mempunyai magnitud yang sama dengan yang disebabkan oleh jerapan GAC, dan keberkesananannya adalah 2x lebih rendah berbanding dengan  $\text{V}^{5+}\text{-TiO}_2$  and  $\text{TiO}_2$  yang disalutkan pada tiub kaca Pyrex. Kinetik tindak balas diperolehi di atas mematuhi tertib tindak balas pseudo pertama mengikut model Langmuir-Hinshelwood. Secara keseluruhannya, degradasi fotopemangkinan MB dengan menggunakan sistem titania adalah paling berkesan apabila  $\text{TiO}_2$  didopkan dengan  $\text{V}^{5+}$  dan disalutkan pada bahan sokong lengai, yang mana tiub kaca Pyrex telah digunakan.



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## ABBREVIATION AND SYMBOLS

Abs	Absorbance
AC	Activated carbon
AOPs	Advanced oxidation processes
GAC	Granular activated carbon
M-TiO <sub>2</sub>	Metal-doped TiO <sub>2</sub>
TiO <sub>2</sub> -GAC	TiO <sub>2</sub> coated on granular activated carbon
M-TiO <sub>2</sub> -GAC	Metal-doped TiO <sub>2</sub> coated on granular activated carbon
MB	Methylene blue
MO	Methyl orange
UV	Ultra-Violet
TiO <sub>2</sub>	Titanium dioxide
e <sub>CB</sub> <sup>-</sup>	Conduction band electron
h <sub>VB</sub> <sup>+</sup>	Valence band hole
λ <sub>max</sub>	Maximum absorbance
k <sub>1</sub>	pseudo-first order kinetic rate constant
BET	Brunauer-Emmet-Teller
SEM	Scanning Electron Micrograph
XRD	X-Ray Diffractogram
% removal	Percentage of MB removal



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## CHAPTER 1

### INTRODUCTION

#### 1.1 An Overview of Advanced Oxidation Processes in Wastewater Treatment

Industrial, agricultural and municipal wastewaters can contain either inorganic (e.g. heavy metals, acids) or organic (e.g. dyes, surfactants, oils, pesticides) pollutants, or a combination of both types of pollutants. The composition of wastewaters, however depends on the type of sources. Continuous discharge of untreated or poorly treated wastewaters into the aquatic environment can cause adverse impacts (Sasawsky *et al.*, 2000; Driscoll *et al.*, 2003). Inputs of the pollutants can lead to degradation in water quality besides causing ecological and health impacts. It is therefore necessary to treat these wastewaters to remove the pollutants prior to discharge. In many countries, such discharges need to attain specific standards in accordance with the environmental regulation. In Malaysia, this requirement is specified under the Environmental Quality Act 1974, specifically under the Environmental Quality (Sewage and Industrial Effluents) Regulations 1979.

A number of physical, biological and chemical methods are available for wastewater treatment. Advanced oxidation processes (AOPs) is one of the chemical methods. This technique have been widely used to treat organic and inorganic pollutants in wastewater, sludge and air (Fujishima *et al.*, 2000; Tan *et al.*, 2003; Charatterjee and Dasgupta, 2005). AOPs use the combination of powerful oxidizing agents and UV light to photodegrade pollutants (Hsing *et al.*, 2007; Malato *et al.*, 2007). AOPs rely mainly on the formation of reactive and short-lived oxygen containing intermediates such as hydroxyl radicals ( $\text{HO}^{\bullet}$ ) and superoxide radicals ( $\text{O}_2^{\bullet-}$ ) which are responsible in the decomposition of pollutants (Yang *et al.*, 2004c; Haque and Muneer, 2007). The pollutants are degraded into  $\text{CO}_2$ , water and mineral-end products such as  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  (Anpo and Takeuchi, 2003; Konstantinou and Albanis, 2004; Kumar *et al.*, 2005).

Over the years AOPs have undergone significant developments. Starting with the basic process of oxidation in the presence of H<sub>2</sub>O<sub>2</sub> and UV, AOPs have evolved to photooxidation involving TiO<sub>2</sub> photocatalyst (Dvoranová *et al.*, 2002; Bahnemann, 2004; Coleman *et al.*, 2005). The TiO<sub>2</sub> photocatalyst used are in the form of suspension (as powdered form) or thin films. Subsequently, metal-doped TiO<sub>2</sub> photocatalysts were introduced. Lately, there have been increasing interests on TiO<sub>2</sub> photocatalyst immobilized on activated carbon adsorbent (Carp *et al.*, 2004; Subramani *et al.*, 2007).

Much of current researches on AOPs are focused on photocatalysis involving TiO<sub>2</sub>. In general, TiO<sub>2</sub> is photoactive under UV light shorter than 400 nm (Agustina *et al.*, 2005; Liu *et al.*, 2008). Under this condition, TiO<sub>2</sub> generates electron-hole pairs, namely electron from conduction band (e<sub>CB</sub><sup>-</sup>) and hole at valence band (h<sub>VB</sub><sup>+</sup>), which subsequently react with H<sub>2</sub>O or O<sub>2</sub> to generate the reactive radicals HO<sup>•</sup>, O<sub>2</sub><sup>•-</sup> and HO<sub>2</sub><sup>•</sup> (Malato *et al.*, 2002; Witmann *et al.*, 2005). Under normal temperature and air pressure, TiO<sub>2</sub> systems in the presence of UV-irradiation could completely degrade most pollutants to harmless compounds (Lu *et al.*, 2008). However, the degradation is more effective in the presence of H<sub>2</sub>O<sub>2</sub> (Kiwi *et al.*, 1993; Halmann, 1996; Oppenländer, 2003).

Studies have also been carried out for the photocatalytic degradation process involving single or multi metal-doped TiO<sub>2</sub> (Yang *et al.*, 2002; Arabatzis *et al.*, 2003; Park *et al.*, 2004; Yang *et al.*, 2004b; Liu *et al.*, 2006a). The transition metals with many valencies are most frequently studied. The metal dopants can be *p*-Type (valencies lower than Ti<sup>4+</sup>) or *n*-Type (valencies higher than Ti<sup>4+</sup>). Examples of *p*-Type dopants include Cu<sup>2+</sup>, Fe<sup>3+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup> ions, whilst *n*-Type dopants are V<sup>5+</sup>, W<sup>6+</sup>, Nb<sup>5+</sup> and Mo<sup>5+</sup> ions (Carp *et al.*, 2004; Park *et al.*, 2004; Li *et al.*, 2007c).

TiO<sub>2</sub> photocatalyst was initially used as suspension in slurry systems (Carp *et al.*, 2004). Due to the problem associated with the need of eventual separation by filtration during post treatment, it is now used in the form of thin films (Alam and Cameron, 2001; Gao and Liu, 2005; Yuan *et al.*, 2007). Recently, instead of the

conventional Pyrex-glass tubes, specific adsorbents were used as support for the thin films. Examples of adsorbents include zeolites, silica, alumina, clay and activated carbon (Carp *et al.*, 2004; Moriguchi *et al.*, 2004; Crini, 2006; Li *et al.*, 2007b; Subramani *et al.*, 2007). Studies using activated carbon as support have reported better photocatalytic degradation compared to conventional TiO<sub>2</sub> thin films (El-Sheikh *et al.*, 2004; Carpio *et al.*, 2005; Liu *et al.*, 2006c; Zhang *et al.*, 2006b; Matos *et al.*, 2007).

The TiO<sub>2</sub> thin film can be prepared according to several methods such as chemical vapour deposition, physical vapour deposition, spray pyrolysis and sol-gel techniques. Each method has its own advantages and disadvantages (Sonawane *et al.*, 2004, Carp *et al.*, 2004). The sol-gel dip-coating method is one of the preferred sol-gel techniques (Sonawane *et al.*, 2004; Du *et al.*, 2005). Sol-gel techniques normally are lower in equipment cost, and can be used to prepare thin films with good homogeneity and at low process temperature (Dong *et al.*, 2002; Zhou, *et al.*, 2004).

## **1.2 Wastewater Treatment by Metal Doped-Titania-Assisted Oxidation Process**

There have been a number of studies involving wastewater treatment using TiO<sub>2</sub> and metal-doped TiO<sub>2</sub>. Some studies reported that metal-doped TiO<sub>2</sub> produced enhanced photocatalytic degradation of pollutants (Arabatzis *et al.*, 2003; Xu *et al.*, 2004; Yang *et al.*, 2004b; Wu *et al.*, 2006), while some reported poor or reduction in photocatalytic activity (Matos *et al.*, 2001; Kemp and McIntyre, 2006). Similar to undoped TiO<sub>2</sub>, the photocatalytic efficiency of the metal-doped TiO<sub>2</sub> photocatalysts also can be influenced by factors such as type of metal dopant, metal to Ti ratio, solution pH, catalyst's concentration, pollutant type, addition and concentration of oxidant (Lee *et al.*, 2004; Li and Li, 2002a; Li *et al.*, 2005a; Senthilkumar *et al.*, 2006; Zhu *et al.*, 2006a).

The addition of metal dopant into TiO<sub>2</sub> can modify the morphology, chemical environment and distribution of the TiO<sub>2</sub> thin films (Arroyo *et al.*, 2002). Metal-doped TiO<sub>2</sub> can also exhibit photocatalytic characteristics under visible light, with

25-32% of solar light absorption (Dvoranová *et al.*, 2002; Teoh *et al.*, 2007). However, it is not as effective as under UV light irradiation (Fujishima and Zhang, 2006).

Both *n*-Type and *p*-Type metal dopants can enhance the photocatalytic activity of TiO<sub>2</sub> (Li and Li, 2002b; Park *et al.*, 2004; Yang *et al.*, 2004b; Xin *et al.*, 2007). However, its' photocatalytic efficiency can be influenced by the concentration of metal-dopant (i.e. the metal to Ti ratio). For example, Yang *et al.* (2004b) showed that the photocatalytic degradation rate constant of methyl orange (MO) by molybdenum-doped TiO<sub>2</sub> increased to 0.054 min<sup>-1</sup> from 0.028 min<sup>-1</sup> with increase in Mo concentration from 0 to 1 mol%. The rate, however, dropped when Mo content exceeded 1 mol% (i.e. 0.03 min<sup>-1</sup> at 1.5 mol %). The optimum metal to Ti ratio, however, can vary according to the type of pollutant. For example, the photocatalytic degradation of XRG yellow dye is most effective when 0.40% Fe<sup>3+</sup>-doped TiO<sub>2</sub> was used (Zhu *et al.*, 2006a) while the degradation of methyl orange (MO) is effective using 4% Fe<sup>3+</sup>-doped TiO<sub>2</sub> (Sonawane *et al.*, 2004).

There have been few researches on photocatalysis using multi-metal-doped TiO<sub>2</sub> (Yang *et al.*, 2002; Zhang *et al.*, 2006a; Xu *et al.*, 2008). The synergistic effect between the metal dopants can enhance the photocatalytic efficiency of TiO<sub>2</sub>. However, the metal to Ti ratio can significantly affect the efficiency of multi metal-doped TiO<sub>2</sub>. For example, TiO<sub>2</sub> co-doped with Fe<sup>3+</sup> and Eu<sup>3+</sup> ions at appropriate ratios, namely 1% Fe<sup>3+</sup> and 0.5% Eu<sup>3+</sup>, shows superior photocatalysis to degrade chloroform in solution compared to undoped TiO<sub>2</sub> (Yang *et al.*, 2002). Low or excessive ratio of metal dopants, however, can significantly retard the photocatalytic reactivity (Carp *et al.*, 2004).

The addition of oxidants such as H<sub>2</sub>O<sub>2</sub> can enhance the photocatalytic activity of metal-doped TiO<sub>2</sub> catalysts (Senthilkumar *et al.*, 2005; Haque and Muneer, 2007). However, excessive H<sub>2</sub>O<sub>2</sub> can decrease the rate of photocatalytic degradation (Fernández *et al.*, 2004; Tryba *et al.*, 2006).

As with undoped TiO<sub>2</sub>, most studies on photocatalytic degradation using metal-doped TiO<sub>2</sub> involved the catalyst being coated as thin films on inert supports namely Pyrex-glass, soda lime glass, fiberglass and glass sheets (Sonawane *et al.*, 2004; Du *et al.*, 2005; Thevenet *et al.*, 2005). Unlike undoped TiO<sub>2</sub>, there have been only a few reports on catalysis involving metal-doped TiO<sub>2</sub> coated on adsorbent materials such as activated carbon (Zhang *et al.*, 2005a; Sun *et al.*, 2006). For example, Sun *et al.* (2006) reported that Sn(IV)/TiO<sub>2</sub>/AC produced greater degradation of Orange G (~2x) as compared with TiO<sub>2</sub>/AC. Meanwhile, Zhang *et al.* (2005a) reported that the degradation of methyl orange (MO) using Ag-doped TiO<sub>2</sub>/AC is at least 1.25x higher than pure TiO<sub>2</sub> and Degussa P25.

### 1.3 Objectives of the Research

This research focuses on photocatalytic degradation of an organic pollutant using metal-doped TiO<sub>2</sub> coated on different support materials, namely Pyrex-glass tube and granular activated carbon (GAC). Methylene blue (MB) was used as the simulated/synthetic pollutant in aqueous solution. The objectives of this research are:

- a) To prepare metal-doped TiO<sub>2</sub> catalyst according to simple sol-gel dip-coating method;
- b) To determine the photocatalytic degradation of MB in the presence of metal-doped TiO<sub>2</sub> coated on Pyrex-glass tube;
- c) To compare MB degradation by metal-doped TiO<sub>2</sub> and undoped TiO<sub>2</sub>;
- d) To compare the photocatalytic degradation of MB in the presence of single-metal-doped TiO<sub>2</sub> and dual-metals-doped TiO<sub>2</sub>;
- e) To determine the photocatalytic degradation of MB in the presence metal-doped TiO<sub>2</sub> coated on GAC.

#### 1.4 Scope of Study

This study investigated the photocatalytic degradation of MB by metal-doped TiO<sub>2</sub> in the presence of UV and H<sub>2</sub>O<sub>2</sub>. The metal-doped TiO<sub>2</sub> were prepared as thin films on Pyrex-glass tubes by sol-gel dip-coating method. The metal dopants used were *n*-Type (Cr<sup>3+</sup>, Cu<sup>2+</sup>, Fe<sup>3+</sup>) and *p*-Type (Mo<sup>5+</sup> and V<sup>5+</sup>). The metal-doped TiO<sub>2</sub> catalysts were single-metal-doped TiO<sub>2</sub> (Cr<sup>3+</sup>-TiO<sub>2</sub>, Cu<sup>2+</sup>-TiO<sub>2</sub>, Fe<sup>3+</sup>-TiO<sub>2</sub>, Mo<sup>5+</sup>-TiO<sub>2</sub>, V<sup>5+</sup>-TiO<sub>2</sub>) and dual-metal-doped TiO<sub>2</sub> (Cr<sup>3+</sup>-Mo<sup>5+</sup>-TiO<sub>2</sub>, Cr<sup>3+</sup>-V<sup>5+</sup>-TiO<sub>2</sub>, Cu<sup>2+</sup>-Mo<sup>5+</sup>-TiO<sub>2</sub>, Cu<sup>2+</sup>-V<sup>5+</sup>-TiO<sub>2</sub>, Fe<sup>3+</sup>-Mo<sup>5+</sup>-TiO<sub>2</sub>, Fe<sup>3+</sup>-V<sup>5+</sup>-TiO<sub>2</sub>, Mo<sup>5+</sup>-V<sup>5+</sup>-TiO<sub>2</sub>). The photocatalytic degradation was also determined using metal-doped TiO<sub>2</sub> coated as thin films on granular activated carbon, M-TiO<sub>2</sub>/GAC, where M-TiO<sub>2</sub> is the metal-doped TiO<sub>2</sub> catalyst (i.e. V<sup>5+</sup>-TiO<sub>2</sub>) with the best degradation rate obtained in the earlier experiments. Comparison was made with undoped TiO<sub>2</sub>, TiO<sub>2</sub>-GAC and GAC systems. The performances of these titania assisted systems in photocatalytic degradation of MB in aqueous solution were evaluated based on the changes in absorbance values at  $\lambda_{\text{max}} = 665 \text{ nm}$ .

